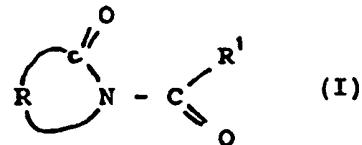




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/39, C07D 227/087		A1	(11) International Publication Number: WO 95/14759 (43) International Publication Date: 1 June 1995 (01.06.95)																		
<p>(21) International Application Number: PCT/GB94/02583</p> <p>(22) International Filing Date: 25 November 1994 (25.11.94)</p> <p>(30) Priority Data:</p> <table> <tr><td>9324261.8</td><td>25 November 1993 (25.11.93)</td><td>GB</td></tr> <tr><td>9325777.2</td><td>16 December 1993 (16.12.93)</td><td>GB</td></tr> <tr><td>9326382.0</td><td>23 December 1993 (23.12.93)</td><td>GB</td></tr> <tr><td>9326385.3</td><td>23 December 1993 (23.12.93)</td><td>GB</td></tr> <tr><td>9326383.8</td><td>23 December 1993 (23.12.93)</td><td>GB</td></tr> <tr><td>9326384.6</td><td>23 December 1993 (23.12.93)</td><td>GB</td></tr> </table> <p>(71) Applicant (for all designated States except US): WARWICK INTERNATIONAL GROUP LIMITED [GB/GB]; Wortley Moor Road, Leeds LS12 4JE (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): CROWTHER, Jan, Darrel [GB/GB]; Vaughn Close, Prestatyn, Clwyd LL19 8SH (GB). HAQUE, Ekram [GB/GB]; 4 Ash View, Aston Park, Hawarden, Deeside, Clwyd CH5 1BL (GB). COLES, Barrie [GB/GB]; Montrose, Pant Asaph, Holywell, Clwyd CH8 8PN (GB).</p> <p>(74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).</p>		9324261.8	25 November 1993 (25.11.93)	GB	9325777.2	16 December 1993 (16.12.93)	GB	9326382.0	23 December 1993 (23.12.93)	GB	9326385.3	23 December 1993 (23.12.93)	GB	9326383.8	23 December 1993 (23.12.93)	GB	9326384.6	23 December 1993 (23.12.93)	GB	<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	
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<p>(54) Title: BLEACHING COMPOSITIONS</p> <p>(57) Abstract</p> <p>Bleach activators and the peroxygen-based oxidising species formed in situ from a peroxygen source and a bleach activator, the bleach activator having formula (I) in which R represents an optionally substituted alkenyl function having at least 2 carbon atoms in the alkenyl chain which forms a cyclic structure with -N- and -C(O)- and R¹ represents a C₁₋₃₀ alkyl or aryl group; or has the formula -R²-COX where X may be OH, OM (where m is a metal ion), -ONR³₄ (where R³ are each independently selected from H and C₁₋₄ alkyl), a halogen atom, amine, C₁₋₃₀ alkyl or alkoxy or a leaving group and R² is a C₁₋₃₀ alkylene or arylene group with the proviso that where R is (CH₂)₅, R¹ represents a C₃₋₉ branched alkyl group or a C₁₀₋₃₀ alkyl or aryl group or a C₉₋₁₀ branched aralkyl group; or has the formula -R²-COX and R² is a C₃₋₁₀ branched alkyl group or C₁₁₋₃₀ alkylene or arylene group, or a C₉₋₁₀ branched alkarylene. Compositions including these bleach activators in combination with conventional bleach activators such as tetraacylated alkylene diamines, particularly TAED or SNOBS give particularly useful cleaning properties.</p>																					



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Bleaching Compositions

This invention relates to the in situ production of peroxygen-based oxidising species from a peroxygen source 5 and an activator followed by the use of the product as an oxidising agent, for instance in a detergent or as a bleach or a biocide.

It is known that percarboxylic acid compounds are 10 useful as bleaching agents, general oxidising agents and biocides. Such compounds may be incorporated into for instance laundry detergents, hard surface cleaners, paper and pulp bleaching compositions, fabric and fibre bleaching compositions and even depilatory creams as well as biocidal compositions, for use in agriculture.

15 It is also known to use a combination of peroxygen bleach precursor (or peroxygen source) and bleach activator in the same or separate compositions to form the oxidising species. The bleach activators are acyl-releasing agents. Suitable bleach activators are O-acyl or N-acyl compounds.

20 However, there is still a need for further bleach activators which will provide good bleaching and may also provide improved cleaning in detergent compositions.

25 In GB 855735 bleaching processes and compositions for textile material are described in which the bleaching composition is an aqueous solution comprising hydrogen peroxide and a reactive acyl organo-amide. A large range of compounds is included in this definition, including N-acyl lactams, of which the only exemplified lactam is N-acetyl caprolactam.

30 GB 1596313 discloses detergents for laundering textiles in which the compositions contain bleaching agents and an activator. The only activator mentioned is N-acetyl caprolactam. N-acetyl caprolactam is also mentioned in GB 2189520 A which relates to washing and bleaching processes.

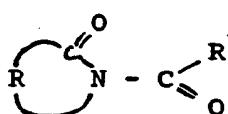
35 A typical example of a bleach precursor is given as N-acetyl caprolactam. Caprolactam in its N-acetylated form

is also known as an ingredient in detergent compositions from SU 1664826.

In EP-A-0122763, bleach compositions are described in which an activator is adsorbed onto sodium perborate monohydrate. The activators claimed are any O-acyl or N-acyl activator and a large range of suitable compounds are disclosed. Within these compounds, N-acyl caprolactam is mentioned, where the acyl group is R^aCO in which R^a represents hydrogen or an alkyl group of chain length C_1 to 5 C_9 aliphatic or aromatic group, optionally substituted by an alkyl or carboxylic acid group or the acyl is a di-acyl 10 derived from a dicarboxylic acid having from 4 to 12 carbon atoms.

The present invention relates to novel bleach 15 activators which provide improved cleaning properties in detergent compositions.

In accordance with the present invention there is 20 provided a bleach activator comprising an optionally substituted N-acyl heterocycle having the formula I:



(I)

25 in which R represents an optionally substituted alkenyl function having at least 2 carbon atoms in the alkenyl chain which forms a cyclic structure with -N- and -C(O)- and R¹ represents a C_{1-30} alkyl or aryl group; or has the 30 formula $-R^2-COX$ where X may be OH, OM (where M is a metal ion), $-ONR^3$, (where R³ are each independently selected from H and C_{1-4} alkyl), a halogen atom, amine, C_{1-30} alkyl or alkoxy or a leaving group and R² is a C_{1-30} alkylene or arylene group with the proviso that where R is $(CH_2)_5$, R¹ 35 represents a C_{3-9} branched alkyl group or a C_{10-30} alkyl or aryl group or a C_{9-10} branched aralkyl group; or has the formula $-R^2-COX$ and R² is a C_{3-10} branched alkyl group or C_{11-30} alkylene or arylene group, or a C_{9-10} branched alkarylene.

Thus, the compounds of the formulae I may be optionally substituted N-acyl 3-membered heterocycles (2-azetidinones) of the formula II:

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10 N-acyl 5-membered heterocycles, N-acyl pyrrolidones having the formula (III):

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they may be N-acyl 6-membered rings of the formula (IV):



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N-acyl 7-membered rings caprolactams of the formula (V):

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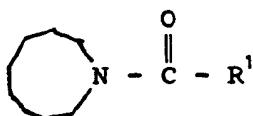
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N-acyl 8-membered heterocycles (2-azocyclooctanones) of the formula (VI):



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or N-acyl 9-membered heterocycles (2-azocyclononanones) of the formula VII:



(VII)

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or N-acyl heterocycles having 10-membered rings or above. In each of the formulae listed above, R¹ is as defined for formula I above.

10 Where the bleach activator is a 7-membered ring, preferably R¹ is a C₁₀₋₂₈, or C₁₂₋₂₆ alkyl group, most preferably R¹ is a C₁₄₋₂₄ alkyl group. Although it is not preferred, R¹ may be a group linked to a substituent on the caprolactam ring to form a cyclic structure. Any branching
 15 may be with C₁ or C₂ groups or alternatively C₃ or above alkyl groups. Where the bleach activator is other than a 7-membered ring, preferably R¹ is a C₂₋₁₄, most preferably C₇₋₁₂ group. Particularly preferred groups are aryl especially phenyl, which are optionally substituted, or alkyl groups,
 20 preferably straight chain, especially ethyl. Although it is not preferred, R¹ may be a group linked to a substituent on the ring formed from -R-, -N- and -C(O)-, to form a cyclic structure.

Particularly preferred activators of the present
 25 invention for compounds of formula (II), (III), (IV), (VI) or (VII) are benzoyl N-substituted heterocycles. In the present invention, unless specified, the term alkyl(ene) includes alkynyl(ene) and alkenyl(ene) groups and these groups may be straight chain, branched or may include
 30 cycloalkyl, or groups. The alkyl groups may include heteroatoms such as N or O in the chain. As used herein, aryl(ene) includes phenyl(ene) and alkaryl(ene). The alkyl(ene) or aryl(ene) may include heterocyclic groups. They may be such substituted such as hydroxyl, lower
 35 alkyl (i.e. up to C₅), amine, substituted amine (especially substituted with C₁₋₃₀, preferably C₁₋₅ alkyl groups), acyl, acyloxy, alkoxy, aryl, aroyl, aryloxy, aroyloxy, halogen, amido, imido groups nitro, sulphonic

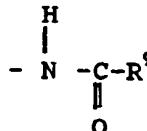
acid and the like they may be alkoxylated with ethers having C₁₋₃₀ alkyl groups, in particular, ethoxylated or propoxylated, or substituted as well as any other groups not adversely affecting the activity of the compound.

5 Where X is a leaving group, suitable leaving groups are for example any group which may be displaced from the bleach activator as a consequence of nucleophilic attack on the bleach activator. Generally leaving groups exert an electron attracting effect and are therefore weak bases.

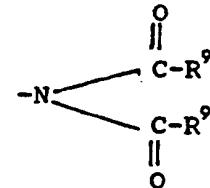
10 Where X is a leaving group it preferably forms a compound the conjugate acid of which has a pKa in the range 4-13, preferably 7-11, most preferably 8-11. Good leaving groups are also those which form a stable entity to minimise the rate of back reaction. Suitable leaving groups include

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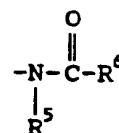
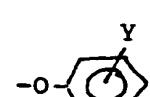
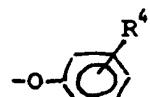
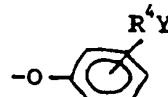
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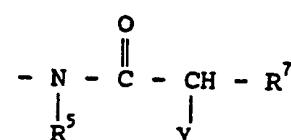
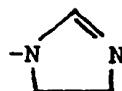
25 and preferred leaving groups include

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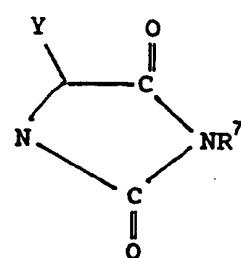
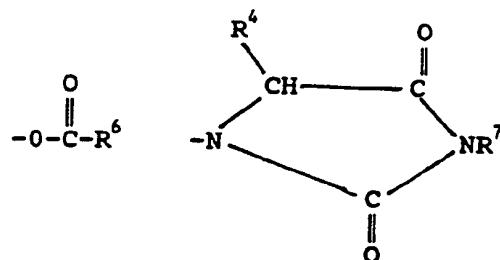


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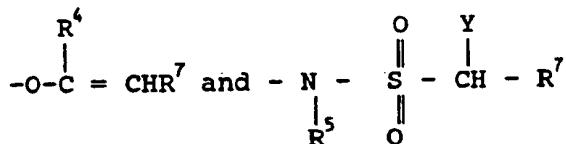
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wherein R^5 and R^6 are hydrogen, or alkyl or aryl, preferably having from 1 to 14 carbon atoms;

R^4 is H or an alkyl chain containing from 1 to 8 carbon atoms;

R^7 is H, alkyl or aryl;

R^9 is alkyl or aryl, preferably having from 1-20, most preferably 1-14 carbon atoms; and

Y is H or a solubilising group.

The preferred solubilising groups in Y are $-\text{SO}_3^-\text{M}^+$, $-\text{COO}^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $(-\text{N}^+\text{R}^8_4)\text{X}_2^-$ and $\text{O}-\text{N}^+(\text{R}^8_4)$

and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{COO}^-\text{M}^+$ wherein R^8 is an alkyl chain containing from 1 to 4 carbon atoms, M^+ is a cation. Preferably, M^+ is a metal ion as described above (M), or ammonium or a substituted ammonium cation, with sodium and potassium being most preferred, and X_2^- is a halide, hydroxide, methylsulfate or acetate anion.

On reaction of a bleach activator of the present invention with a peroxygen source, a more active bleaching species which may be a peracid is formed, in addition to unsubstituted heterocycle. Useful examples of bleach activators according to formula I include 5-membered ring heterocycles as defined in formula I where R is $-\text{CH}_2\text{R}'_3$ and R' is a phenyl, 4-methylphenyl, 4-nitrophenyl, 4-tertiary butylphenyl, 1-ethylphenyl, 3-pyridyl, pentyl, 4-chlorophenyl, 4-methoxyphenyl, octyl, phenoxyethyl, 2-nitrophenyl, 3-nitrophenyl or tertiary butyl group;

7-membered ring heterocycles as defined in formula I where R is $-\text{CH}_2\text{R}'_5$ and R' is 3,4 dicarboxyphenyl anhydride, 4 - tertiarybutyl phenyl, tertiary butyl, 5-(N-

phthalimidyl)pentyl, tridecyl, phenoxyethyl, 3-(N,N-dimethylamino)phenyl, 4-(N,N-dimethylamino) phenyl, 1-ethylpentyl or heptadecyl;

5 8-membered ring heterocycles of formula I where R is $\text{CH}_2\text{CH}_2\text{CH}_2$ and R' is methyl or phenyl.

The present invention also includes a bleaching composition comprising one or mixtures of more than one of the bleach activators as defined above.

In the present invention the term "bleaching" is 10 intended to include any process where the solution is used to remove or reduce unwanted colour in a substrate and/or reduce or remove non-coloured stains from fabric substrate and/or act as a disinfectant and the term "bleaching composition" is exemplified by but not limited to 15 detergents, especially laundry detergents, dishwashing detergents, hard surface cleaners, including kitchen and bathroom cleaners, toilet cleaners, pipe cleaners, dry bleaches, compositions for bleaching wood, paper and pulp bleaching compositions, fabric and fibre bleaching 20 compositions and oral hygiene compositions including mouthwashes, toothpastes and plaque-removing compositions and depilatory creams. In such bleaching compositions, there is included a precursor peroxygen source, that is a composition which releases perhydroxyl groups (OOH^-).

25 The precursor peroxygen source may be hydrogen peroxide itself, but is alternatively an inorganic salt for instance a percarbonate or a perborate. Sodium or potassium salts are preferred, such as sodium perborate, or an organic peroxide such as benzoyl peroxide or urea 30 peroxide.

Alternatively, bleaching compositions according to the invention may be used in conjunction with separate compositions which comprise such a bleach precursor.

35 The invention also includes a process in which a peroxygen source is reacted with one of the above activator compounds in aqueous solution to form a product solution

containing an oxidising product and the product solution is used as a bleach.

Where the peroxygen source is hydrogen peroxide itself, the concentration of hydrogen peroxide is 5 preferably less than 70% (weight/volume) that is weight of hydrogen peroxide based on volume of water plus hydrogen peroxide plus other components in the mixture). Preferably the concentration is less than 60% weight by volume and more preferably less than 30% w/v. Where the product of 10 the reaction is to be used in a domestic environment or other environment where it is difficult to take special precautions in handling the product, it is preferred for the concentration to be less than 15 or even less than 10% w/v. The concentration is usually at least 1% w/v more 15 preferably at least 2% w/v.

Where the peroxygen source is other than hydrogen peroxide the concentration is preferably such as to give the equivalent available oxygen as the quoted concentrations of hydrogen peroxide. The concentration of 20 peroxygen source in the aqueous liquid is for instance less than 10 M, preferably less than 5 M or sometimes even less than 3M down to 0.01 M. Preferably the concentration is at least 0.1M more preferably at least 0.2M. During the reaction, the temperature is preferably in the range 0 to 25 95°C, more preferably in the range 10 to 80°C, for instance in the range 20 to 60°C. The temperature in any subsequent oxidising step is preferably in the same ranges as the temperature during the reaction of the peroxygen source and the activator compound and is preferably substantially the 30 same temperature specifically where the product solution is used for instance as a bleach or disinfectant. A particular advantage of using activators for the peroxygen source is that the oxidising product tends to be formed at a relatively low temperature, for instance 40°C or less, or 35 even less than 30°C or 25°C which is advantageous for both safety and energy.

The compositions of the present invention are particularly useful in detergents, especially laundry detergents for both natural and synthetic fibres.

Generally, the reaction between the peroxygen source and the activator will take place under alkaline conditions, above pH 7 or 7.5. However, the reaction may also take place under acidic conditions. Generally the pH for the reaction will be from 6 to 14. Preferably it will be above 7.5 or even 8 and most preferably the pH will be from 9.5 to 12.5. Generally the bleaching compositions will be alkaline at a pH above 7.5. However, the composition may also contain a pH-modifier which may comprise an acid, a base and/or buffering material so that the desired pH can be obtained for the reaction between the precursor and the activator. For example, when the pH-modifier is an acidifying pH-modifier, it may comprise a polybasic organic acid such as a polybasic carboxylic acid, for example citric, succinic, adipic or sulphonic acid. Alternatively the pH-modifier may react with a by-product of the perhydrolysis reaction of the peroxygen source with the activator compound to produce an acid or base. Where perborate is used, borate is a by-product and so any component known to react with perborate to produce acidity for example a polyol, boric acid or sodium di-hydrogen phosphate can be used to provide the pH-modifier.

In the composition of the present invention, the peroxygen source and the activator compound may be provided in separate compositions. For instance, the peroxygen source may be in the form of an aqueous solution of peroxygen whilst the activator may be provided in the solid form. However, preferably the components are provided in a stable composition, which is preferably therefore substantially water free.

The composition may be in liquid form, for instance in a non-aqueous liquid medium, in which the components may be dissolved or dispersed. For instance particles of activator with protective coatings, for instance produced

by micro-encapsulation techniques or spray coating of solid activator, may be suspended in an aqueous, or non aqueous, solution of peroxygen source. As an alternative to a solution of peroxygen source that component may also be 5 suspended in the liquid medium, either in a separate liquid phase or in particulate dispersed phase, particles of solid peroxygen source optionally being coated with a protective coating. Coated particles of either peroxygen source or activator may be disrupted or diluted into water or with 10 abrasion.

Preferably the composition (or compositions) is in solid form, for instance as a mixture of particles of the individual components or, more preferably, comprising particles each of which comprise all of the components. 15 Such particles may be provided by techniques the same or similar to those conventionally used in the laundry detergent industry, for instance including particles produced by spray drying liquid slurries, by granulation techniques using binders (for instance synthetic or natural 20 polymers or derivatives) or by melt blending followed by extrusion or other techniques.

Preferably the composition contains the active ingredients in appropriate relative quantities so that when the composition is diluted (or the compositions are mixed) 25 with water the first step of the reaction proceeds at the optimal rate and at the desired pH. The activator and peroxygen source are for instance present in relative amounts such that 5% to 150% of the stoichiometric amount of activator (for complete reaction with the peroxygen 30 source) is provided. Preferably the amount of activator is 10 to 100%, more preferably 20 to 80% of the stoichiometric amount.

The new composition may include other additives, for instance stabilisers which stabilise the product before 35 use, as well as stabilisers for the peroxy acid oxidising species formed in the reaction, especially heavy metal sequestrants. The new product may also include surfactants

to act as wetting agents and inorganic salts, for instance which affect the physical properties of the solid form or act as diluent. Other ingredients may be included depending on the final application of the reaction product,
5 for instance perfumes, or agents to assist dissolution or dispersion of the product into water.

The N-substituted heterocyclic bleach activator of formula I may be simply admixed directly in with the other detergent composition compounds. Alternatively it could be
10 coformulated with builders (for example phosphates, polyphosphates, sodium carbonate, silicates, zeolites, clays, borax) complexing or sequestering agents (ethylenediamine tetraacetic acid, diethylenepentamine pentaacetic acid, nitrilotriacetic acid, citrates, phosphonates), enzymes, surfactants (linear alkylbenzene sulphonates, phenol sulphonates, alcohol ether sulphates, alcohol ethoxylates, amphoteric and cationic surfactants),
15 soap, polyacrylates, hydrotropes, mineral oil and foam regulators.

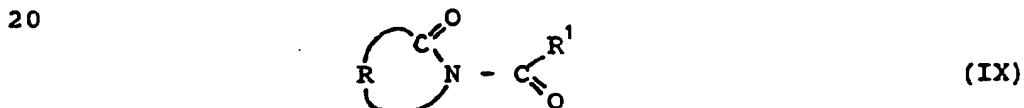
20 The reaction product of the peroxygen source and the activator is preferably used immediately, without removal of any by-products or addition of other materials. Sometimes it may be desirable to add additional ingredients to the composition after the reaction between the peroxygen
25 source and bleach activator such as pH-adjusters, wetting agents, additives to improve the action of the bleaching agent produced in the reaction, for instance co-disinfectants, biocides, abrasives etc.

30 The invention has been found to be surprisingly advantageous when the composition of the present invention comprises a peroxygen source and an N-substituted heterocycle of formula I as defined above, in combination with a conventional activator. The compositions have been found to exhibit enhanced bleaching effects. The
35 compositions are especially effective as laundry detergents for both natural and synthetic fibres. Suitable conventional activators include any compound or mixture of

compounds already known as useful bleach activators. Particularly preferred conventional activators are tetraacylated alkylene diamines such as TAMD or TAED, tetraacylated glycol urils especially TAGU (tetraacetyl glycol uril), pentaacylated glucose, especially PAG (pentaacetyl glucose) and acylated (preferably C_{6-14}) oxybenzene sulphonates, especially SNOBS (sodium nononoyl oxybenzene sulphonate).

It has been found that compositions incorporating both one or more of the N-acyl caprolactam activators of the present invention and a tetraacylated alkylene diamine, preferably TAED have particularly improved detergency properties.

In accordance with a further aspect of the present invention there is provided a bleaching composition comprising a peroxygen source, a conventional bleach activator, preferably a tetraacylated alkylene diamine and a bleach activator of the formula IX:



25 in which R represents an alkenyl function having at least 2 carbon atoms in the alkenyl chain which forms a cyclic structure with -N- and -C(O)- and R' represents a C_{1-30} alkyl or aryl group or has the formula $-R^2-COX$ where X is as defined for formula I above, and R^2 is a C_{1-30} alkylene or 30 arylene group. Preferably R' is a C_{7-30} most preferably C_{7-15} group, or has the formula $-R^2-COX$ where X is as defined above and R^2 is a C_{7-30} group. Preferably R' or R^2 is straight chain alkyl(ene) or aryl(ene) group. Preferably R is a C_5 group or a C_3 group. Preferably R is an 35 unsubstituted alkylene group, eg. $-(CH_2)_5$ or $(CH_2)_3$.

A particularly preferred R' or R^2 group is an optionally substituted aryl(ene) group especially substituted phenyl(ene) group. A further preferred group includes bleach activators having the formula I above and

in which R^1 represents a C_{10-30} or has the formula $-R^2-COX$ where X is as defined above R^2 is a C_{11-30} alkyl group and R comprises from 2 to 7 $-CH_2-$ groups. Without wishing to be bound by theory, it is postulated that the particular advantages which have been found for a combination of the N-acyl bleach activators of formula IX and I with acylated alkylene diamines, and in particular TAED, are due to the short chain nature of the peroxygen bleach compound produced using the alkylene diamine resulting in good hydrophilicity and the relatively long chain peroxygen bleach compounds formed from the activator of the present invention producing good hydrophobicity. Thus, the combination of the two activators used in combination gives good cleaning properties.

15 In a further embodiment of the invention, the conventional activator to be used in combination with the activator as defined in formula IX above comprises SNOBS (sodium nonanoyloxy benzene sulphate). In this embodiment of the invention, it is particularly preferred that the 20 SNOBS is in combination with a bleach activator having the formula IX or I above, in which R^1 represents a C_{1-9} , more preferably C_{2-6} alkyl group or has the formula $-R^2-COX$ where X is as defined above and R^2 is a C^{1-10} alkyl(ene) group, preferably a C_{2-6} alkyl group and R is a C_{2-7} group, 25 preferably alkylene in which the CH_2 groups of the lactam are unsubstituted. Preferably, the activator according to formula I given above is one in which R is a C_5 group and R^1 represents a C_{3-8} branched alkyl group.

Where the composition comprises at least two bleach 30 activators, the first being a bleach activator of formula IX, preferably the activator of formula IX is present in an amount of at least 50% by weight total bleach activator, more preferably at least 70%, or even at least 80 or 90% by weight total bleach activator.

35 The invention is particularly directed to the manufacture of detergents for example used in washing

laundry and the compositions therefore preferably include conventional surfactants.

The novel bleach activators of the present invention can be prepared by any conventional organic synthesis route. They may be prepared by reacting the unsubstituted heterocycle with an acid chloride in which the acyl group is the desired acyl group for N-substitution on the unsubstituted heterocycle. The reaction is preferably carried out under alkaline conditions in a suitable organic solvent such as toluene. The reaction product can be crystallised or precipitated out of the solvent medium.

The invention is illustrated by way of the following examples:

Example 1

15 Preparation of 4-nitrobenzoyl 2-pyrolidone.

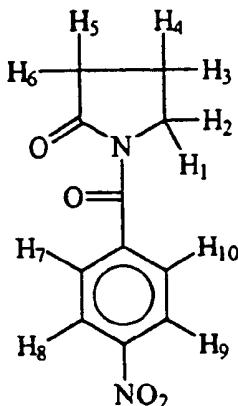
A two litre flat-flanged flask equipped with thermometer, stirrer, dropping funnel and reflux condenser was charged with 292.0g of toluene, 2.78 mol of 2-pyrolidone and 3.00 mol triethylamine. Separately, 2.78 mol 4-nitrobenzoyl chloride was dissolved in 400g of toluene and this mixture was added drop-wise to the contents of the reaction flask at room temperature. Once the addition was completed, the contents of the flask were refluxed for 4 hours. The reaction mixture was then cooled to room temperature and washed with 2 x 100cm³ water to remove the amine hydrochloride. The mixture was then filtered to give the first crop of product. A second crop of product may be obtained from the toluene layer if required by recrystallisation. The yield of 4-benzoyl 2-pyrolidone was 474.2g (72.9%). The melting point of the product was 127-129°C and the purity as measured using HPLC was 98.7%. An NMR spectra of the product was obtained and the results were as follows:

(1) doublet of doublets at around 8ppm (8.25 ppm and 7.70 ppm) indicative of 4-di-substituted aromatic hydrogen atoms (H₇-H₁₀).

(2) quintuplet centred at around 2.17ppm (H₃ and H₄).

(3) triplet centred at 3.98 ppm (H_1 and H_2).
 (4) triplet centred at 2.62 ppm (H_5 and H_6).

5



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An IR spectra of the product was obtained giving results: 2 bands at 1746cm^{-1} and 1666cm^{-1} , respectively, 20 which are indicative of the two carbonyl bonds associated with cyclic imides.

Performance Testing

The bleach activator prepared in example 1 and several 25 other bleach activators of the present invention as listed in Table 1, were tested for washing performance, comparisons being made using: (i) a blank incorporating no bleach activator and (ii) a comparative known bleach activator.

30 Swatches of 100% cotton 12cm x 12cm were stained using the stains listed below:

	WIL Tea	Tea prepared by Warwick International Group Limited
35	BC1	Tea stains with clay
	BC2	Coffee stains
	BC3	Tea stains
	BC4	Curry stains

AS4 Chlorophyll stains

These stains are useful to give an indication of the bleaching power of formulations incorporating bleach activator. AS4 is particularly good at indicating 5 bleaching performance on oily stains.

Wash tests were carried out under conditions typical of both European and U.S. laundry washing conditions. European wash tests were carried out at each of 40°C and 10 60°C, using cold fill Wascator FOM 71 MP machines, programmed to BS 4923 (HLCC) wash programmes. U.S. wash tests were carried out at 40°C only, using Maytag (A7500 Model) or Whirlpool machines (Super Capacity Model 3LA5580XS).

For the European wash tests, formulations 15 incorporating the activator for testing were prepared containing 22.5g PBS4 (sodium perborate tetrahydrate), 124.5g IEC standard base detergent and a weight of activator calculated to give the same moles peracid release as 2% by weight TAED. Formulations were dosed at 7.5g/l 20 wash water via the dispensing drawer of the machines.

For the U.S. wash tests a wash cycle of 12 minutes duration was used, the temperature of the incoming water being 40°C. Formulations contained 5% by weight activator 25 for testing (100% active) 10% PBS1 (sodium perborate monohydrate) and IEC to 100%. The formulations were dosed at 1.5g/l.

During the wash tests the swatches were tagged to 2.5kg polyester backing cloth, using plastic tags. After 30 washing the swatches were removed and ironed dry prior to reading reflectance measurements to assess stain removal. Stain removal was assessed as a percentage brightness and calculated using the equation.

$$35 \quad \text{Stain removal} = \frac{(RA - RB)}{(RS - RB)} \times 100$$

where RA is the reflectance of the washed swatch, RB is the reflectance of the unwashed swatch and RS is the

reflectance of an unstained swatch. Reflectance was measured with U.V. at 420nm using a Spectroflash 500 Spectrophotometer machine.

Due to variations in swatch make up all evaluations 5 were run compared to a TAED or NBC (N-benzoyl caprolactam) or other conventional activator standard, as well as a blank incorporating no activator.

Table 1

Compound	R Group	R' Group	M.Pt (°C)	Purity (HPLC)
A	(CH ₂) ₃	phenyl	80-91	99.7
5	B	(CH ₂) ₃	4-methylphenyl	130-131
	C	(CH ₂) ₃	4-nitrophenyl	130-131
	D	(CH ₂) ₃	4-tert-butylphenyl	104.8-105.9
	E	(CH ₂) ₃	pentyl	liquid
	F	(CH ₂) ₃	4-chlorophenyl	112.5-114.5
10	G	(CH ₂) ₃	4-methoxyphenyl	119.7-120.1
	H	(CH ₂) ₃	octyl	liquid
	I	(CH ₂) ₃	phenoxyethyl	-
	J	(CH ₂) ₅	3,4-dicarboxyphenyl anhydride	-
	K	(CH ₂) ₅	4-tert-butylphenyl	84
15	L	(CH ₂) ₅	tert-butyl	liquid
	M	(CH ₂) ₅	5-(N-phthalimidyl) pentyl	gel
	N	(CH ₂) ₅	phenoxyethyl	75
	O	(CH ₂) ₆	phenyl	-
				97.4

20 The results for the wash tests carried out on each of the bleach activators listed in table 1 above, are given in the tables below. In order to ensure that any effect on the results obtained due to variations in water quality could be minimised, for each set of tests run at the same time, a standard and a blank test were also run. The results in the tables below are given in blocks of tests which were carried out at the same time.

25 30 The results in tables 2 to 4 below illustrate the effective bleaching properties obtained using the bleach activators of the present invention under the washing conditions tested.

Compound	Wash Test Results (European Washes @ 40°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	27.9	4.0	11.9	3.7	12.4	31.3
TAED	32.8	9.0	17.4	13.8	12.9	32.0
NBC	37.8	13.4	24.0	18.6	14.5	36.2
A	32.5	10.5	21.7	16.4	16.3	34.6
B	31.7	11.2	22.6	20.2	13.8	39.9
C	38.6	14.6	24.9	24.0	16.3	36.9
Blank	32.0	8.0	14.0	12.9	22.5	22.6
TAED	33.6	10.0	17.8	20.8	21.2	22.3
NBC	41.4	13.1	23.0	28.0	25.3	25.7
D	31.3	10.0	20.2	21.3	22.1	30.7
Blank	29.5	4.9	5.4	8.8	11.6	16.5
TAED	32.6	5.7	7.1	13.9	12.0	17.1
NBC	32.2	9.6	8.7	16.7	14.0	19.1
E	33.6	6.1	7.0	13.0	10.1	19.0
F	36.0	10.7	10.7	20.4	13.6	23.5
Blank	25.7	12.7	12.2	23.2	13.3	19.2
TAED	29.4	12.0	12.9	22.6	13.4	15.5
NBC	31.9	15.2	14.9	24.9	12.6	15.9
G	26.8	15.4	13.8	26.9	14.9	19.5
H	24.1	8.5	10.2	19.8	7.1	17.0
Blank	35.2	4.1	5.1	13.6	10.7	25.1
TAED	40.9	8.4	8.6	21.6	10.3	24.9
NBC	39.6	8.7	8.6	22.6	13.5	27.6
I	32.1	7.4	6.4	20.6	12.2	22.2

TABLE 2 (contd)

Compound	Wash Test Results (European Washes @ 40°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	30.1	3.6	11.8	5.0	13.6	33.3
TAED	33.6	8.4	17.6	13.8	13.6	32.5
J	38.4	8.0	16.7	9.9	8.4	33.4
Blank	32.0	8.0	14.0	12.9	22.5	22.6
TAED	33.6	10.0	17.8	20.8	21.2	22.3
NBC	41.4	13.1	23.0	28.0	25.3	25.7
K	34.1	9.6	19.1	19.6	20.3	29.8
L	32.0	10.7	19.4	20.3	22.5	24.5
Blank	25.7	12.7	12.2	23.2	13.3	35.1
TAED	29.4	12.0	12.9	22.6	13.4	24.8
NBC	31.9	15.2	14.9	24.9	12.6	15.9
M	22.7	10.7	10.6	18.3	12.2	27.3
Blank	35.2	4.1	5.1	13.6	10.7	25.1
TAED	40.9	8.4	8.6	21.6	10.3	24.9
SNOBS	39.6	8.7	8.6	22.6	13.5	27.6
N	38.6	12.6	11.3	29.9	12.6	26.3
Blank	35.2	4.1	5.1	13.6	10.7	25.1
TAED	40.9	8.4	8.6	21.6	10.3	24.9
NBC	39.6	8.7	8.6	22.6	13.5	27.6
O	38.0	10.2	8.2	23.9	10.3	26.1

TABLE 3

Compound	Wash Test Results (European Washes @ 60°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	38.6	10.5	18.6	16.1	26.3	44.6
TAED	48.7	18.2	29.4	27.8	25.4	46.4
NBC	44.5	21.2	31.9	31.1	33.2	49.0
A	43.1	17.6	31.7	28.5	31.7	49.7
B	47.3	21.2	36.7	32.2	30.1	52.4
C	53.3	24.5	40.0	37.4	33.1	53.9
Blank	43.0	12.2	23.1	29.5	31.8	32.3
TAED	54.8	18.9	30.8	37.5	34.9	35.0
NBC	54	20.3	35.8	41.9	39.6	41.8
D	46.6	18.9	35.2	38.3	42.5	49.6
Blank	40.1	10.7	11.3	23.1	21.3	22.5
TAED	45.4	14.1	14.4	30.4	23.7	23.9
NBC	46.7	15.3	16.7	35.5	24.4	27.1
E	48.2	13.3	14.7	33.2	23.3	25.9
F	46.0	17.2	18.3	38.9	26.2	30.8
Blank	31.9	19.3	15.0	31.7	19.7	29.7
TAED	40.1	21.8	20.2	37.2	20.2	29.4
NBC	41.3	21.4	22.2	38.1	24.8	33.9
G	40.3	22.8	23.7	37.7	26.4	31.7
H	31.9	18.7	17.2	30.0	22.3	30.4
Blank	36.9	11.1	9.8	28.1	22.2	29.9
TAED	43.3	12.4	12.5	34.2	22.0	31.5
NBC	47.7	16.2	16.3	40.1	26.8	34.8
I	40.3	11.8	12.5	32.6	20.6	32.6

TABLE 3 (contd)

Compound	Wash Test Results (European Washes @ 60°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	38.5	10.6	21.9	19.2	25.1	46.3
TAED	50.3	17.6	31.1	28.8	27.6	44.3
J	49.1	11.4	23.0	19.5	24.1	43.2
Blank	43.0	12.2	23.1	29.5	31.8	32.3
TAED	54.8	18.9	30.8	37.5	34.9	35.0
NBC	54.7	20.3	35.8	41.9	39.6	41.8
K	44.6	19.3	36.5	40.1	41.2	51.5
L	51.5	18.4	32.9	38.5	37.2	38.7
Blank	31.9	19.3	15.0	31.7	19.7	47.4
TAED	40.1	21.8	20.2	37.2	20.2	42.8
SNOBS	41.3	21.4	22.2	38.1	24.8	33.9
M	34.3	17.0	16.2	29.0	19.6	46.4
Blank	36.9	11.1	9.8	28.1	22.2	29.9
TAED	43.3	12.4	12.5	34.2	22.0	31.5
SNOBS	47.7	16.2	16.3	40.1	26.8	34.8
N	n/t	n/t	n/t	n/t	n/t	n/t
Blank	36.9	11.1	9.8	28.1	22.2	29.9
TAED	43.3	12.4	12.5	34.2	22.0	31.5
NBC	47.7	16.2	16.3	40.1	26.8	34.8
O	45.5	15.3	15.3	36.0	25.7	35.0

TABLE 4

Compound	Wash Test Results (US Washes @ 40°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	10.1	0.2	5.0	0.7	7.7	7.3
TAED	15.5	3.7	6.3	2.4	8.9	8.4
NBC	13.0	4.3	8.8	2.2	8.4	15.3
A	15.0	4.4	8.2	2.2	10.9	13.6
B	9.8	4.3	8.5	3.2	10.2	15.1
C	15.1	4.9	8.9	4.1	11.1	11.5
Blank	10.9	2.3	2.9	-2.3	18.6	5.3
TAED	17.0	2.9	6.3	0.3	15.3	5.9
NBC	11.8	4.6	7.9	-0.5	17.8	5.6
D	7.3	3.9	5.6	-1.8	19.1	8.8
Blank	21.0	2.3	3.1	6.2	8.3	11.0
TAED	28.3	3.8	3.9	9.4	7.6	11.3
SNOBS	23.4	4.3	5.7	11.9	11.1	14.6
E	25.7	4.4	3.8	4.6	7.7	12.2
F	24.0	6.1	4.5	10.3	8.2	13.0
Blank	17.6	5.9	5.9	8.6	6.6	9.1
TAED	23.5	11.3	7.9	9.2	7.8	12.5
SNOBS	18.5	5.5	6.9	9.0	3.4	12.0
G	19.4	10.0	8.8	9.2	6.3	5.0
H	19.0	8.8	5.9	5.8	9.7	9.3
Blank	25.8	1.6	2.4	6.4	7.2	19.4
TAED	32.0	4.5	2.9	7.8	10.2	19.1
SNOBS	29.3	6.1	5.8	10.0	9.2	25.7
I	29.3	3.5	3.3	6.3	11.9	20.0

TABLE 4 (contd)

Compound	Wash Test Results (US Washes @ 40°C)					
	WIL TEA	BC1	BC2	BC3	BC4	AS4
Blank	8.6	0.3	6.9	1.7	11.2	9.9
TAED	17.6	3.4	4.7	2.2	11.4	10.9
SNOBS	17.3	5.0	11.5	1.5	18.8	21.9
J	17.3	2.3	5.2	1.9	9.7	8.4
Blank	10.9	2.3	2.9	-2.3	18.6	5.3
TAED	17.0	2.9	6.3	0.3	15.3	5.9
NBC	11.8	4.6	7.9	-0.5	17.8	5.6
K	6.2	2.5	3.6	-1.5	15.8	7.4
L	5.5	3.2	4.5	-0.7	14.1	6.4
Blank	17.6	5.9	5.9	8.6	6.6	9.1
TAED	23.5	11.3	7.9	9.2	7.8	12.5
SNOBS	18.5	5.5	6.9	9.0	13.4	12.0
M	11.2	6.8	6.9	7.2	3.9	2.7
Blank	25.8	1.6	2.4	6.4	7.2	19.4
TAED	32.0	4.5	2.9	7.8	10.2	19.1
SNOBS	29.3	6.1	5.8	10.0	9.2	25.7
N	26.5	4.5	2.5	6.0	9.1	18.6
Blank	25.8	1.6	2.4	6.4	7.2	19.4
TAED	32.0	4.5	2.9	7.8	10.2	19.1
SNOBS	29.3	6.1	5.8	10.0	9.2	25.7
O	23.8	1.9	-1.1	4.1	7.9	19.4

CLAIMS

1. A bleach activator comprising an optionally substituted N-acyl heterocycle having the formula I:

5



10 in which R represents an optionally substituted alkenyl function having at least 2 carbon atoms in the alkenyl chain which forms a cyclic structure with -N- and -C(O)- and R' represents a C₁₋₃₀ alkyl or aryl group; or has the formula -R²-COX where X may be OH, OM (where M is a metal ion), -ONR³, (where R³ are each independently selected from H and C₁₋₄ alkyl), a halogen atom, amine, C₁₋₃₀ alkyl or alkoxy or a leaving group and R² is a C₁₋₃₀ alkylene or arylene group with the proviso that where R is (CH₂)₅, R' represents a C₃₋₉ branched alkyl group or a C₁₀₋₃₀ alkyl or aryl group or a C₉₋₁₀ branched aralkyl group; or has the formula -R²-COX and R² is a C₃₋₁₀ branched alkyl group or C₁₁₋₃₀ alkylene or arylene group, or a C₉₋₁₀ branched alkarylene.

15 2. A bleach activator according to claim 1 comprising an optionally substituted compound having the formula II:

20 25



30 in which R' is as defined in claim 1.

3. A bleach activator according to claim 1 comprising an optionally substituted compound of formula III:

35



in which R' is as defined in claim 1.

4. A bleach activator according to claim 1 comprising an optionally substituted compound of formula IV:

40



in which R¹ is as defined in claim 1.

5. A bleach activator according to claim 1 comprising an optionally substituted compound of formula V

5



in which R¹ is as defined in claim 1.

6. A bleach activator according to claim 1 comprising an

10

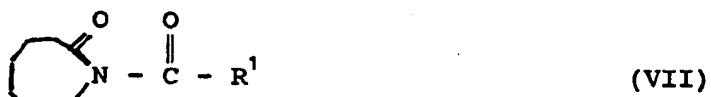
optionally substituted compound of formula VI

15



7. A bleach activator according to claim 1 comprising an optionally substituted compound of formula VII

20



in which R¹ is as defined in claim 1.

8. A bleach activator according to any preceding claim in

which R¹ is an optionally substituted phenyl group, preferably nitrophenyl.

9. A process in which a peroxygen source is reacted with an activator compound according to any preceding claim in a perhydrolysis step in an aqueous solution to form a product solution containing an oxidised product and the product solution is used as a bleach.

10. A composition containing a peroxygen source and an activator according to any of claims 1 to 3.

11. A composition according to claim 10 which is a laundry detergent.

35 12. A bleaching composition comprising a peroxygen source and at least two bleach activators, at least one of the bleach activators comprising a bleach activator of the formula IX:

40



in which R represents an alkenyl function having at least 2 carbon atoms in the alkenyl chain which forms a cyclic structure with -N- and -C(O)- and R¹ represents a C₁₋₃₀ alkyl or aryl group or has the formula -R²-COX where X is OH, OM (where M is a metal ion), -ONR³, (where R³ are each independently selected from H and C₁₋₄ alkyl), a halogen atom, amine, C₁₋₃₀ alkyl or alkoxy or a leaving group as defined for formula I above, and R² is a C₁₋₃₀ alkylene or arylene group.

5 13. A bleaching composition according to any of claims 10 to 12 comprising a tetra-acylated ethylene diamine, preferably TAED.

10 14. A bleaching composition according to any of claims 10 to 13 comprising SNOBS.

15

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/02583

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/39 C07D227/087

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 400 971 (FLORIDA STATE UNIVERSITY) 5 December 1990 see abstract ---	1,2,8
X	WO,A,87 04429 (UPJOHN CO.) 30 July 1987 see page 29, line 24 - line 30; example 1; table 1 ---	1,2
X	EP,A,0 412 058 (SIGMA-TAU IND.) 6 February 1991 see abstract; claim 1 ---	1,3,8
X	EP,A,0 268 218 (NELSON RESEARCH & DEV.) 25 May 1988 see page 5, line 7 - line 39 ---	1,3-5
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
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- *'&' document member of the same patent family

1 Date of the actual completion of the international search

24 March 1995

Date of mailing of the international search report

10.04.95

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INTERNATIONAL SEARCH REPORT

Intern'l Application No
PCT/GB 94/02583

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 113 735 (V.P. KURKOV) 12 September 1978 see claims ---	1,3
X	DE,A,26 16 993 (BAYER AG) 27 October 1977 see page 13; example 16 ---	1,4,5
A	GB,A,1 596 313 (BOSCH-SIEMENS HAUSGERÄTE GMBH) 26 August 1981 cited in the application see the whole document ---	1,5,9-11
E	WO,A,95 00626 (PROCTER & GAMBLE) 5 January 1995 see claims ---	1,4,8-14
E	WO,A,94 28102 (PROCTER & GAMBLE) 8 December 1994 see claims; example 6 -----	1,5,8-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/02583

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0400971	05-12-90	US-A- AU-B- AU-A- CA-A- CN-A- CN-A- JP-A- NO-C- OA-A- PL-B- US-A-	5175315 630696 5515090 2016951 1057049 1086512 3086860 174099 9740 163946 5336785	29-12-92 05-11-92 20-12-90 30-11-90 18-12-91 11-05-94 11-04-91 16-03-94 30-11-93 31-05-94 09-08-94
WO-A-8704429	30-07-87	AU-A- EP-A- EP-A-	6849687 0232017 0282492	14-08-87 12-08-87 21-09-88
EP-A-0412058	06-02-91	AT-T- DE-D- DE-T- ES-T- JP-A- US-A-	110363 69011781 69011781 2058874 3024054 5102896	15-09-94 29-09-94 05-01-95 01-11-94 01-02-91 07-04-92
EP-A-0268218	25-05-88	AU-B- AU-A- DE-A- JP-A- US-A-	607951 8132587 3778833 63150230 4886783	21-03-91 26-05-88 11-06-92 22-06-88 12-12-89
US-A-4113735	12-09-78	US-A-	4151171	24-04-79
DE-A-2616993	27-10-77	FR-A- GB-A- JP-A-	2348311 1559627 52128477	10-11-77 23-01-80 27-10-77
GB-A-1596313	26-08-81	DE-A- FR-A,B SE-B- SE-A-	2719235 2388924 439504 7802908	09-11-78 24-11-78 17-06-85 30-10-78

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/02583

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9500626	05-01-95	AU-B-	7061794	17-01-95
WO-A-9428102	08-12-94	AU-B-	6833394	20-12-94

